Recrystallization of barite in the presence of Radium – a microscopic and spectroscopic study

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Introduction:

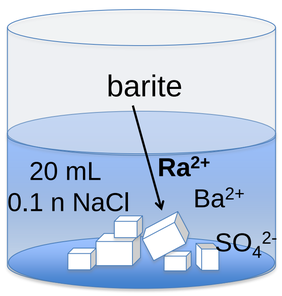
The uptake of Ra by barite via solid solution formation is controlling the solubility of Ra in aqueous systems. Under nuclear waste repository relevant conditions, Ra may enter a system in which barite is in equilibrium with the aqueous solution. For the uptake of Ra by existing solid barite, previous macroscopic studies have suggested that barite may partially or fully recrystallize to $(Ba_{1-x}Ra_x)SO_4$ solid solution [1,2], i.e. Ra uptake is not limited to pure adsorption.

Objectives:

- Does barite take up Ra during recrystallization?
- Does barite completely recrystallize into a $Ba_{1-x}Ra_xSO_4$ solid solution in the presence of Ra?
- Spatial distribution of Ra within the solid?
- Influence of the presence of Ra on the recrystallization of barite?
- Influence of barite morphology and particle size distribution?

Experimental setup:

- Batch recrystallization experiments at **room temperature (RT).**
- **Sachtleben barite (SL)**: blocky crystals, particle size of > 10 µm.
- **Aldrich 99.99 % barite (AL)**: rounded, agglomerates, smooth crystal surfaces, particle size < 2 µm
- The **solid/liquid ratio: 5 g/L** and **0.5 g/L.**
- Initial Ra/Ba ratio of 0.3 (**$5*10^{-6}$ mol/L Ra**).



Experimental setup.

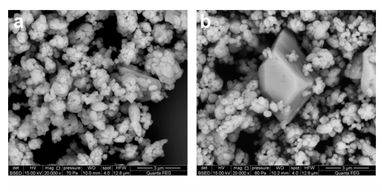
Methods:

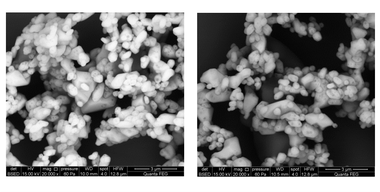
- The morphological evolution of the barite crystals was investigated by **SEM**.
- The **grain size distribution** was determined by image analysis of SEM images.
- **ToF-SIMS** measurements were performed, in order to investigate the spatial distribution of Ra within the barite.

Results and discussion:

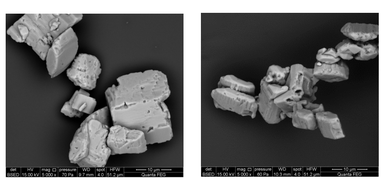
Morphology & Grain Size Distribution:

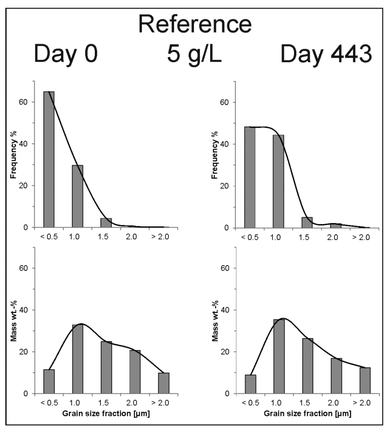
Aldrich

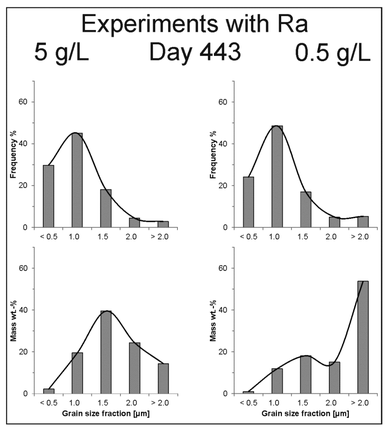


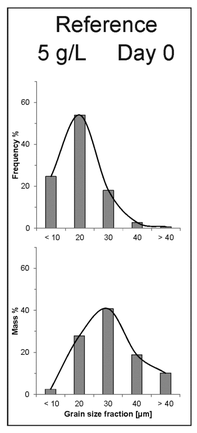


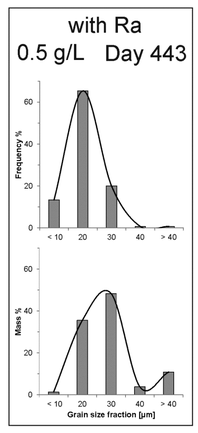
Sachtleben



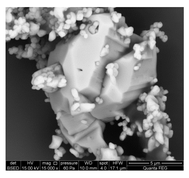








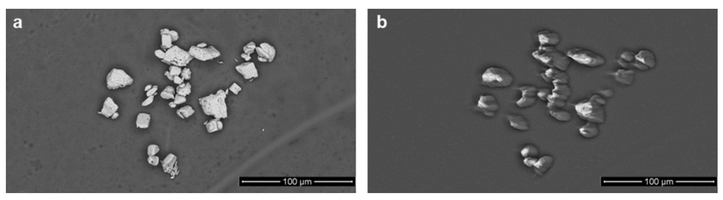
	Minimum	Maximum	Mean value	
			Frequency based	Equ. mass based
	[µm]	[µm]	[µm]	[µm]
AL Reference at the beginning	0.19	2.20	0.50	0.69
AL Reference 5 g/L after 443 days	0.19	2.97	0.58	0.82
AL 5 g/L after 443 days	0.28	3.58	0.80	1.15
AL 0.5 g/L after 443 days	0.25	3.59	0.86	1.26
360 grains per sample analyzed				
	[µm]	[µm]	[µm]	[µm]
SL Reference at the beginning	5.62	44.65	15.00	18.62
SL 5 g/L after 443 days	5.46	38.13	15.28	18.79
SL 0.5 g/L after 443 days	5.91	44.64	14.99	18.33
150 grains per sample analyzed				



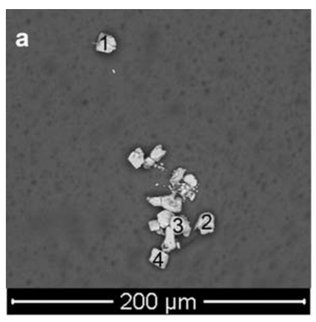
Newly formed large crystal of AL after 443 days in the presence of Ra.

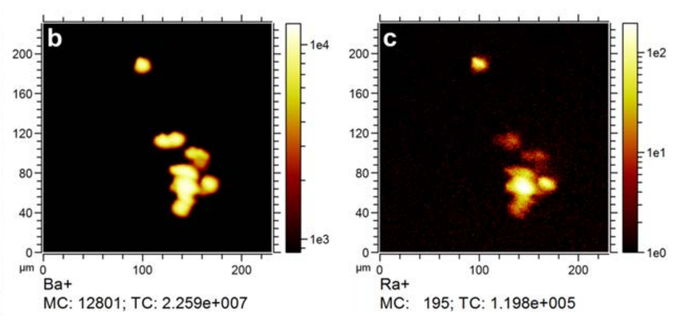
- Morphology:
  - AL: Large idiomorphous crystals with smooth plain crystal faces appear; small particles show a less rounded shape, sharp edges, and less pores on the surface
  - SL: Formation of large aggregates; no significant change of the morphology; smoother crystal faces
- Grain size distribution:
  - AL: Grain coarsening due to Ostwald ripening after recrystallization without Ra; significant additional influence of Ra on the coarsening
  - SL: Slight effects on the grain size distribution
- Ra catalyses the recrystallization of barite

Element Distribution by ToF-SIMS:

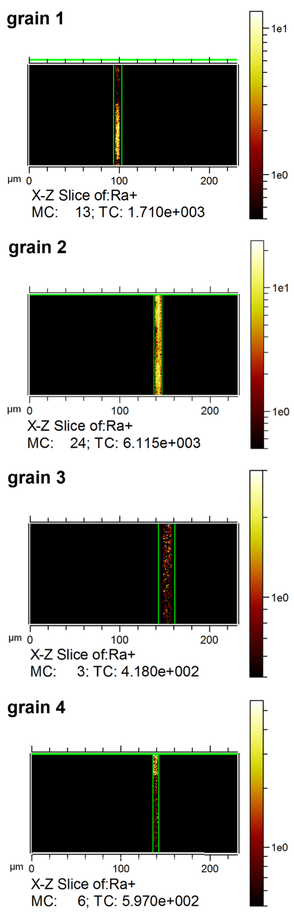


Powder samples before (a) and after ToF-SIMS measurement (b).



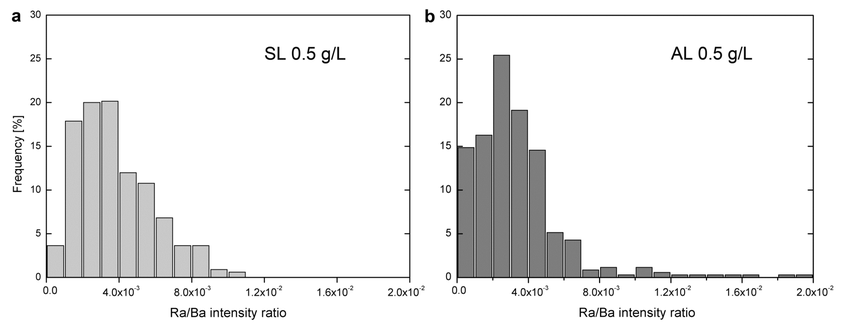


SL 0.5 g/L before measurement (a) Integrated intensities of Ba (b) and Ra (c) signals.
MC: max. counts
TC: total counts



Depth profiles of the integrated Ra signal (resolution ~ 0.1 µm).

Name	Type of barite	Solid/Liquid [g/L]	Final Ra concentration [mol/L]	X_{RaSO4} solid [-]
SL 0.5 g/L	Sachtleben	0.5	$3.5 \times 10^{-08} \pm 1.0 \times 10^{-8}$	2.5×10^{-3}
SL 5 g/L	Sachtleben	5	$2.8 \times 10^{-09} \pm 0.8 \times 10^{-9}$	2.5×10^{-4}
AL 0.5 g/L	Aldrich	0.5	$4.7 \times 10^{-08} \pm 1.4 \times 10^{-8}$	2.5×10^{-3}
AL 5 g/L	Aldrich	5	$7.4 \times 10^{-09} \pm 2.2 \times 10^{-9}$	2.5×10^{-4}



Histograms of the Ra/Ba intensity ratio obtained from 660 integrated measurement points of SL 0.5 g/L (a) and of AL 0.5 g/L obtained from 350 integrated measurement points (b).

- After 443 days, SL 0.5 g/L and 5 g/L barite contain **Ra in the crystal volume**.
- Indication of **complete recrystallization** of barite to $Ba_{1-x}Ra_xSO_4$ solid solution.
- Calculated Ra/Ba ratios from macroscopic results correspond well to ToF-SIMS results.

Outlook:

Spectroscopic and microscopic (e.g. TEM) studies will be carried out to achieve a nanoscopic system understanding of the micro structural evolution and Ra incorporation into the barite crystal as well as its spatial distribution in the crystal.

Acknowledgment:

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References:

[1] Bosbach, D.; Böttle, M. & Metz, V. (2010) *Waste Management, Svensk Kärnbränslehantering AB*
[2] Curti, E. et al. (2010) *Geochimica et Cosmochimica Acta*, **74**, 3553-3570